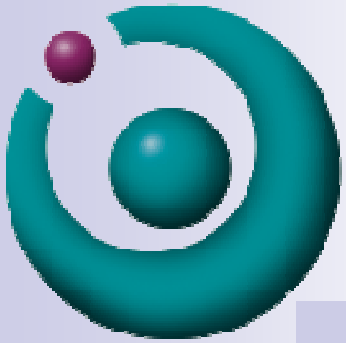


Use of Light Emitting Diodes in the Visible Region to Initiate Polymerisation leading to Monolithic Stationary Phases

Zarah Walsh, Dominik Heger, Silvija Abele, Petr Klán, Brett Paull, Pavel A. Levkin, Frantisek Svec and Mirek Macka

Outline

- The current state of the art of monolith synthesis
- The advantages of working in the visible region
- The benefits of working with LEDs
- My research
  - Part I: Initiation at 660 nm
  - Part II: Initiation at 470 nm
- Conclusions

Initiation of monolith synthesis: State of the art

Thermal initiation
All standard moulds
Long polymerisation times
No spatial control

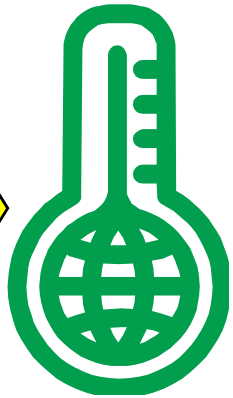
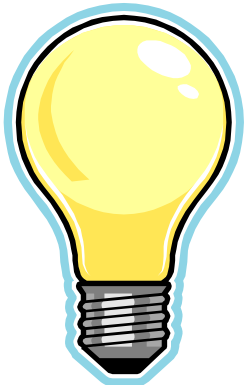


Photo initiation
Light transparent moulds
Short polymerisation times
Excellent spatial control



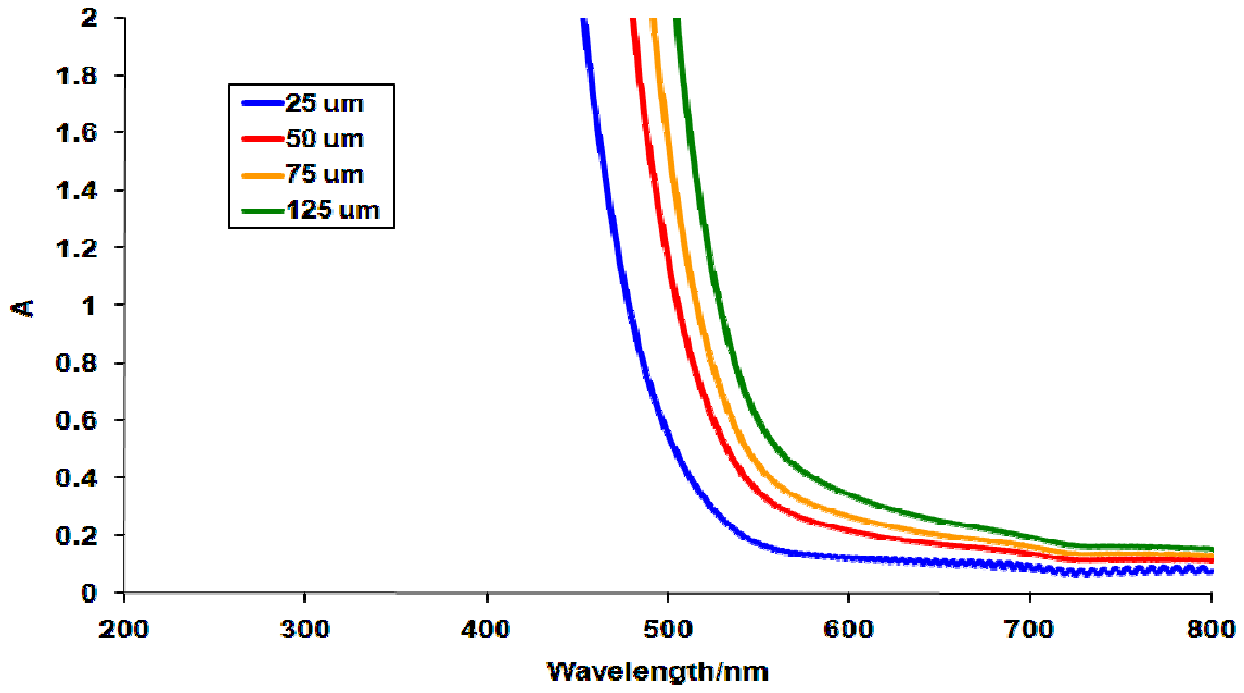
Gamma radiation initiation
All standard moulds
Short polymerisation times
No spatial control

Microwave initiation
All standard moulds
Short polymerisation times
No spatial control

Electron beam initiation
All standard moulds
Short polymerisation time
No spatial control

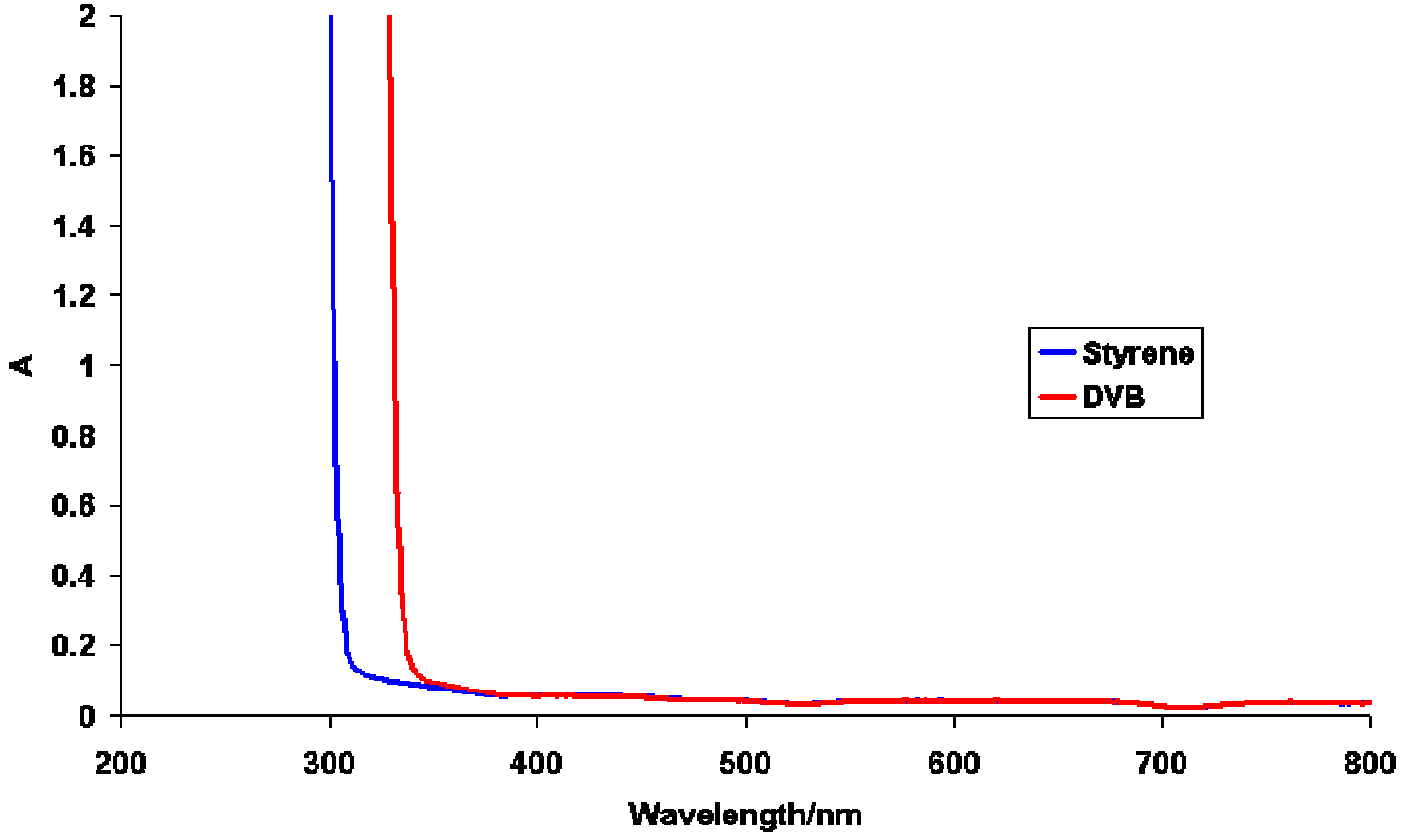
Advantages of working in the visible region….

- Polyimide does not absorb strongly above 550 nm so polyimide coated capillaries can be used as a mould



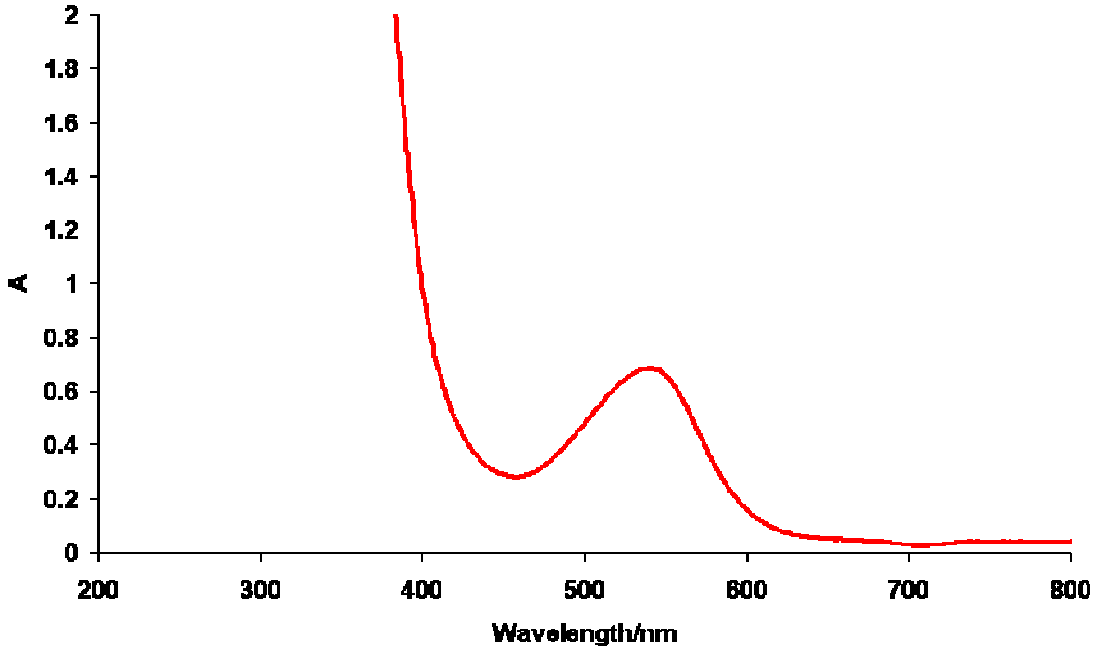
Advantages of working in the visible region….

- Styrenes don't absorb in the visible region

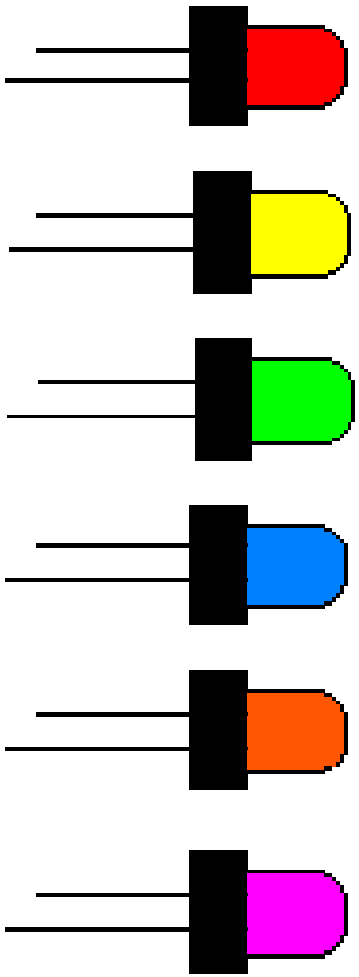


Advantages of working in the visible region….

- Monomeric dyes, while absorbing strongly in the UV, usually don't absorb throughout the whole visible region



The Use of LEDs



Cheap

Small and Robust

Quasi-monochromatic; no need for filters

Long lifetime; >100,000 h

High intensity LEDs are available

Heat generation is negligible

LEDs already used to initiate bulk polymerisations [1]

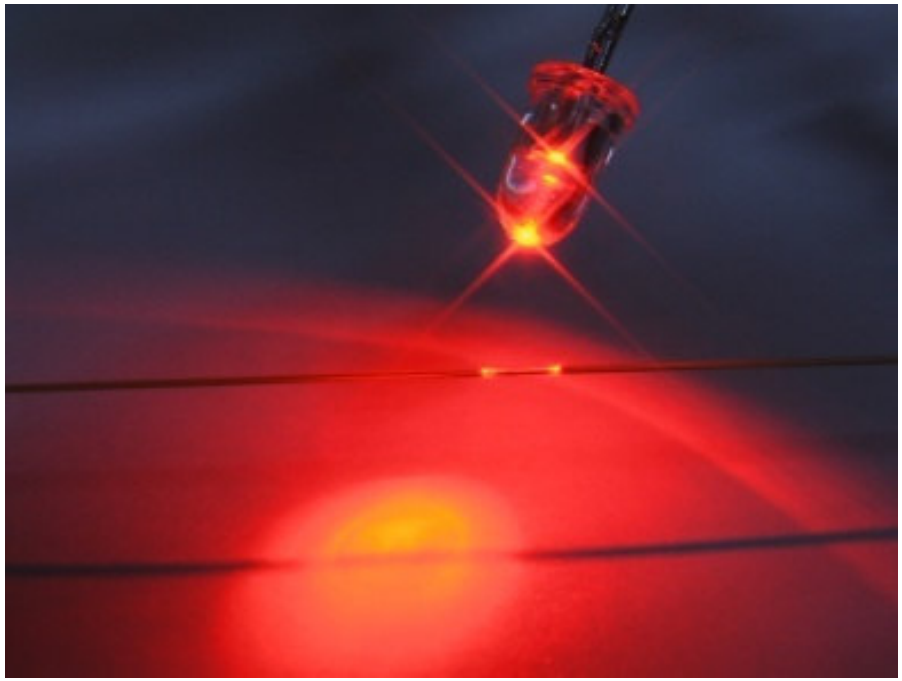
Now used to initiate polymerisation within capillaries [2, 3]

[1] McDermott *et al.*, ***Optics and Laser Technology***, 40, **2008**, 487

[2] Abele *et al.*, ***Analyst***, 133, **2008**,

[3] Walsh *et al.*, ***Chem.Comm.***, 48, **2008**, 6504

Part I: Initiation at 660 nm

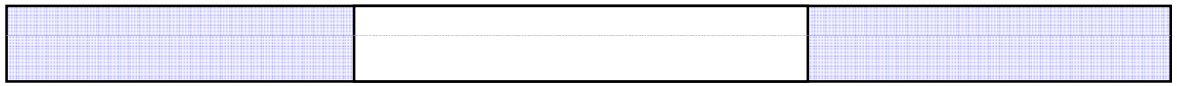


Walsh *et al.*, ***Chem.Comm.*** 48, 6504-6506, **2008**

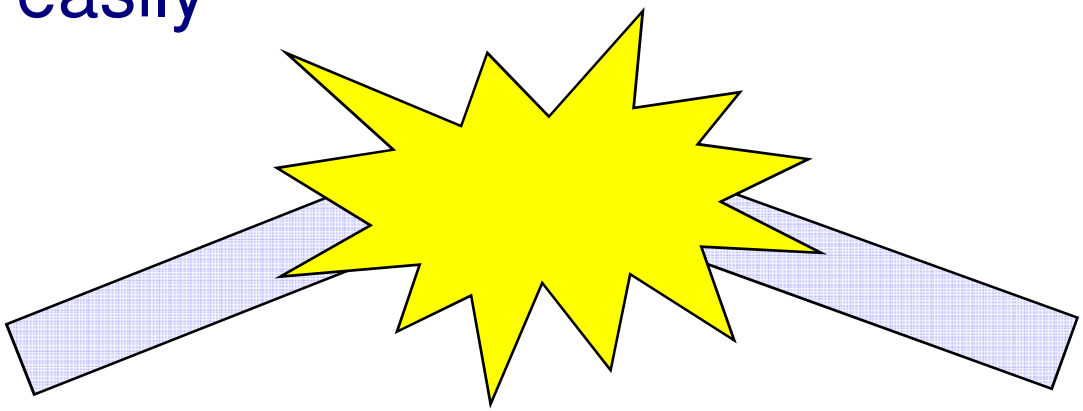
- Polymerisation of methacrylate monoliths within polyimide coated capillaries with 660 nm LEDs and a cyanine/borate initiator complex

Identification of a problem

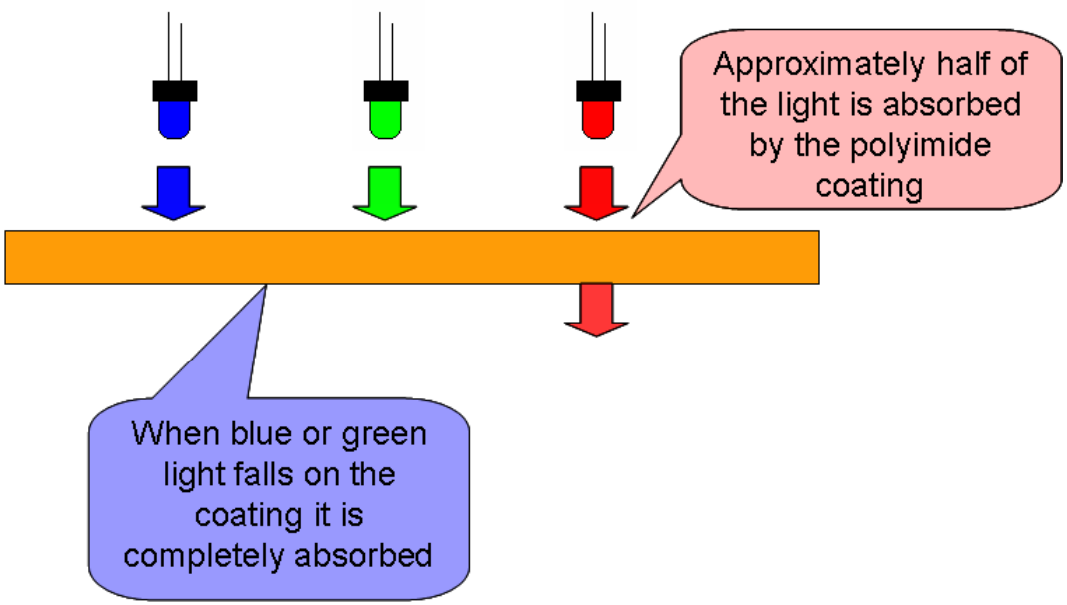
- Photoinitiated polymerisation can be done easily with UV light in PTFE coated capillary….



- However, this capillary is quite brittle and can break easily



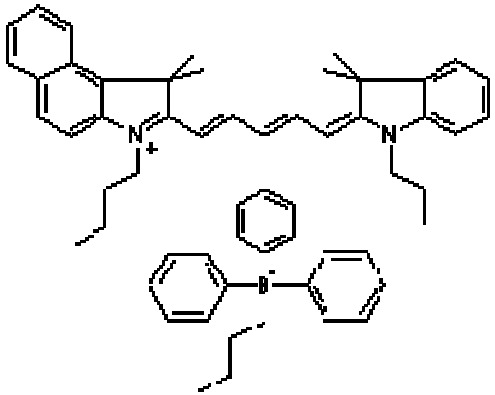
Polyimide makes the capillary more durable…



- While it becomes more durable, it also becomes less transparent
- Only in the red region of the spectrum does the light pass more easily through the capillary into the internal cavity

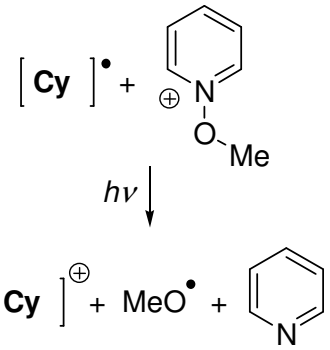
Selection of the Initiator

- Initiator absorbing above 550 nm is necessary



λ_{max} = 660 nm

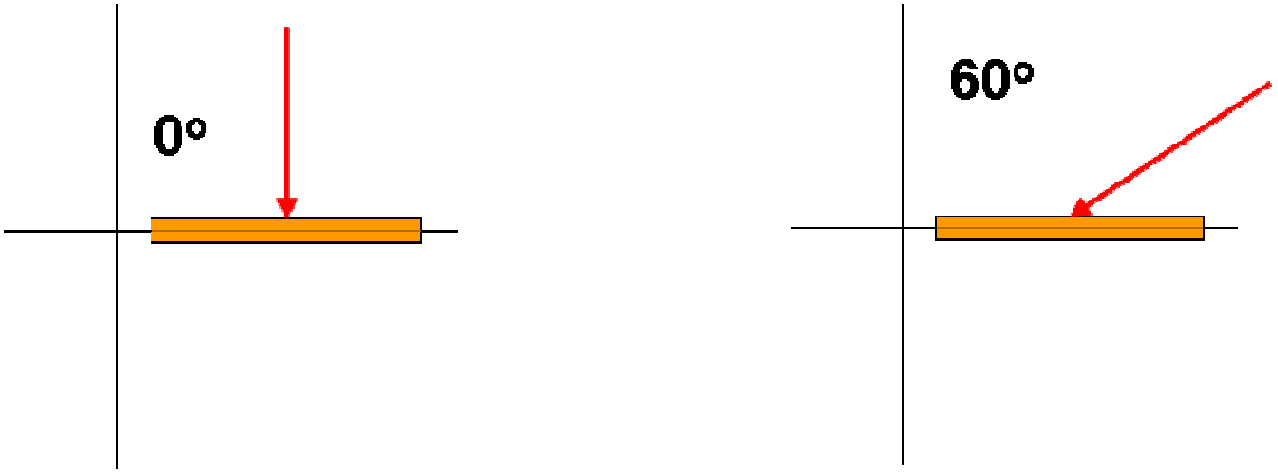
- Radicals generated very slowly = long polymerisation time



Quick reaction!

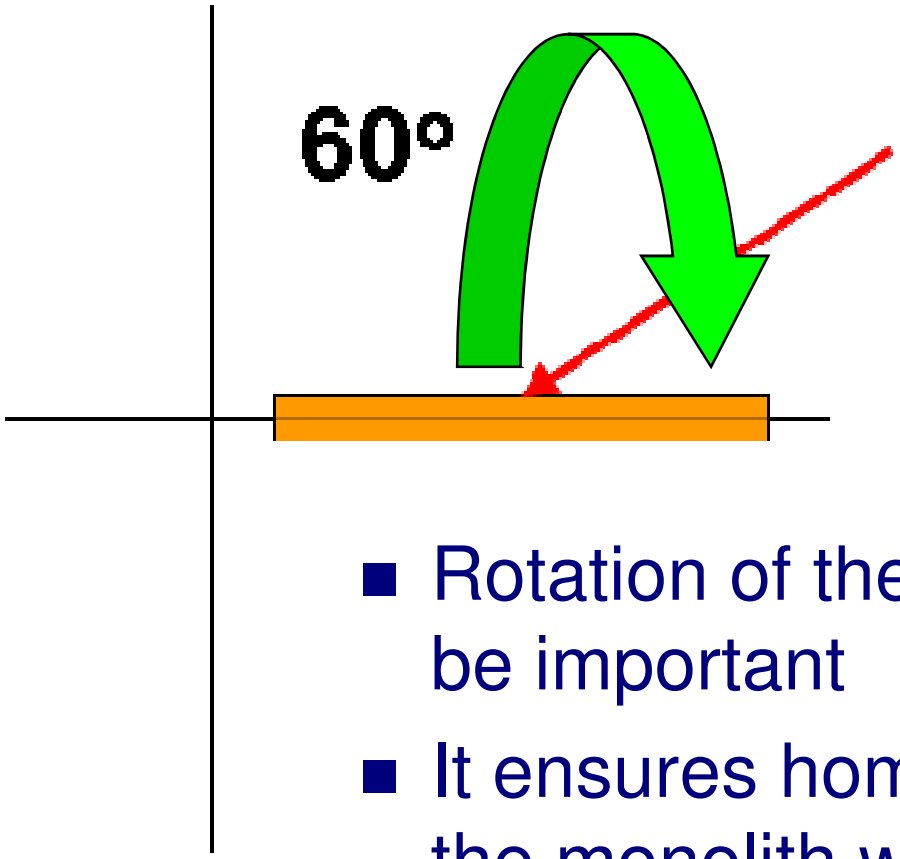
20 – 120 min

Angle of the capillary relative to the LED



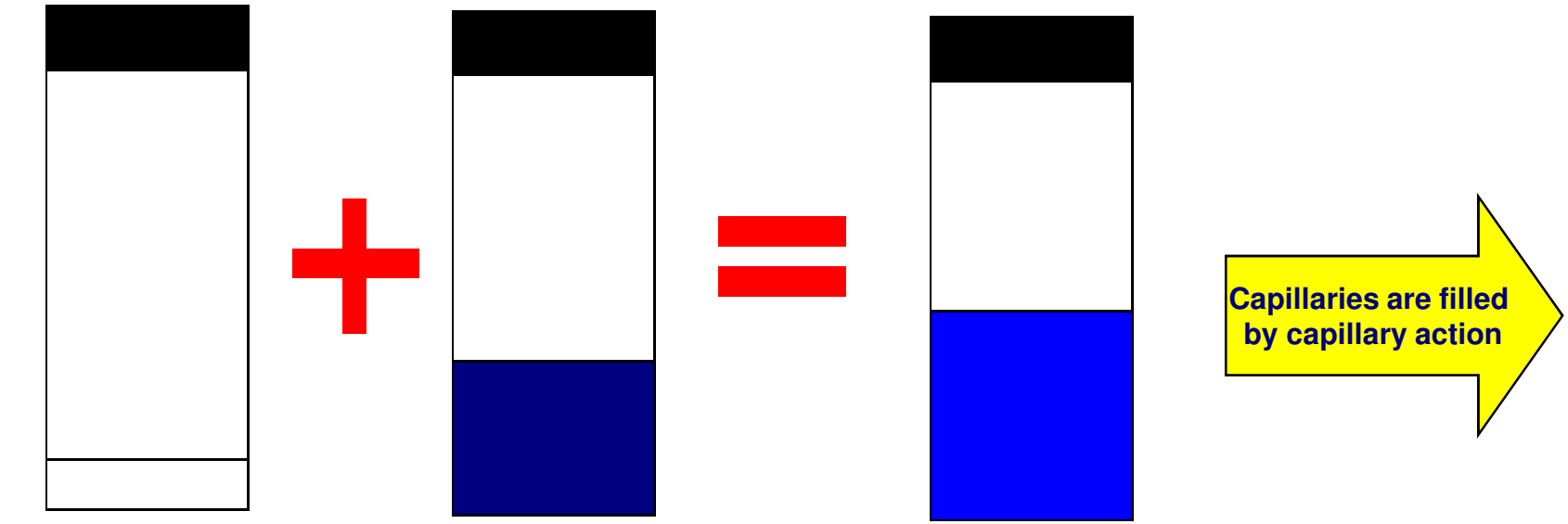
- Perpendicular position creates only one focal point
- Position at 60° creates multiple focal points
- This means more light within the cavity

Rotation of the capillary



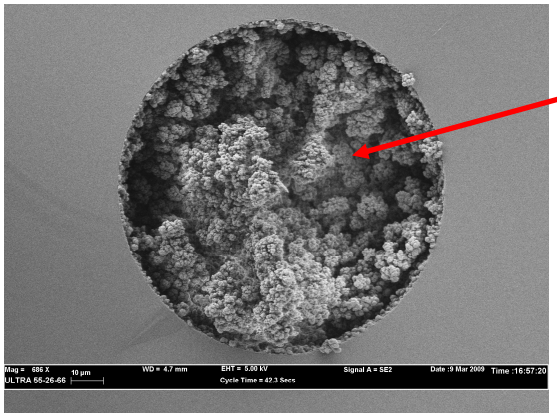
- Rotation of the capillary was found to be important
- It ensures homogeneous distribution of the monolith within the capillary

Polymerisation Conditions

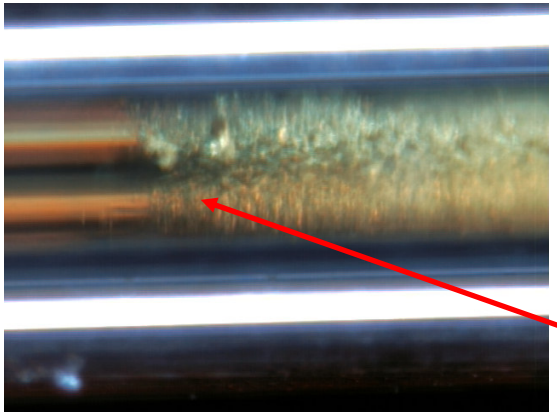


Monomer + cross-linker	Initiator + co-initiator + ACN, 1-propanol, 1-decanol	Polymerisation solution

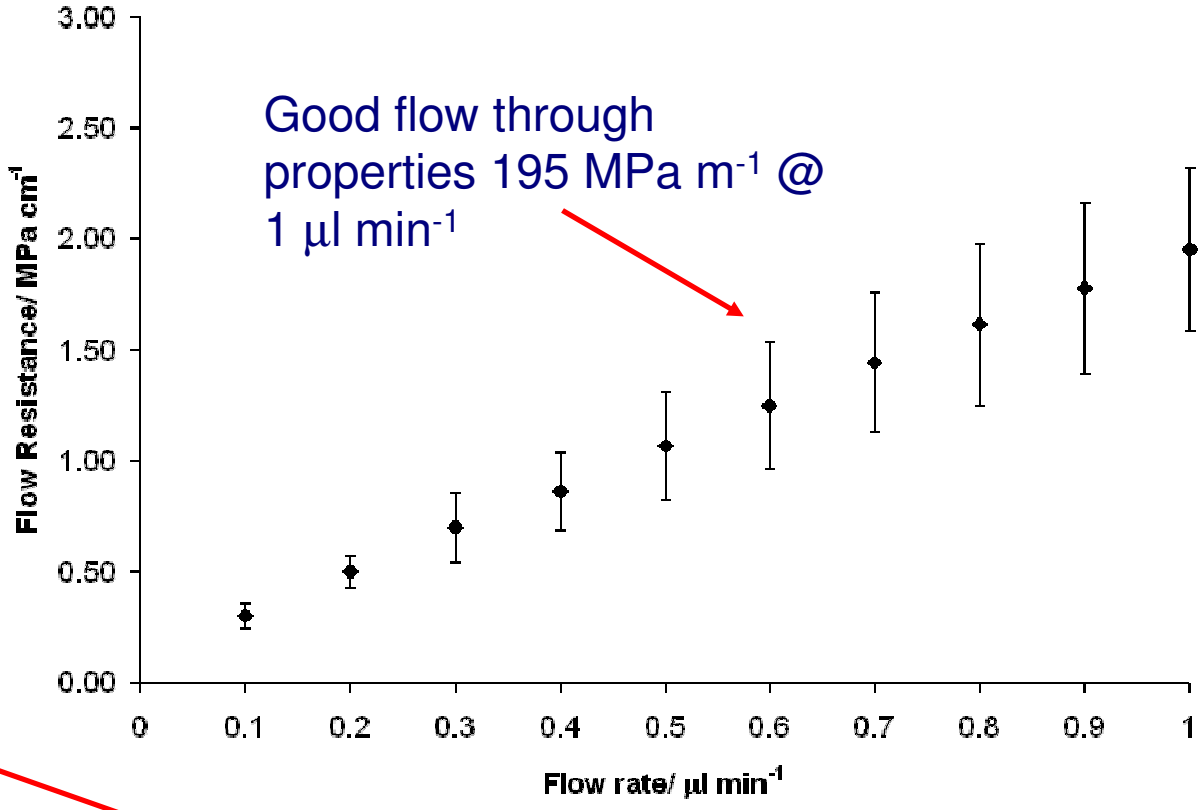
Characterisation of monoliths



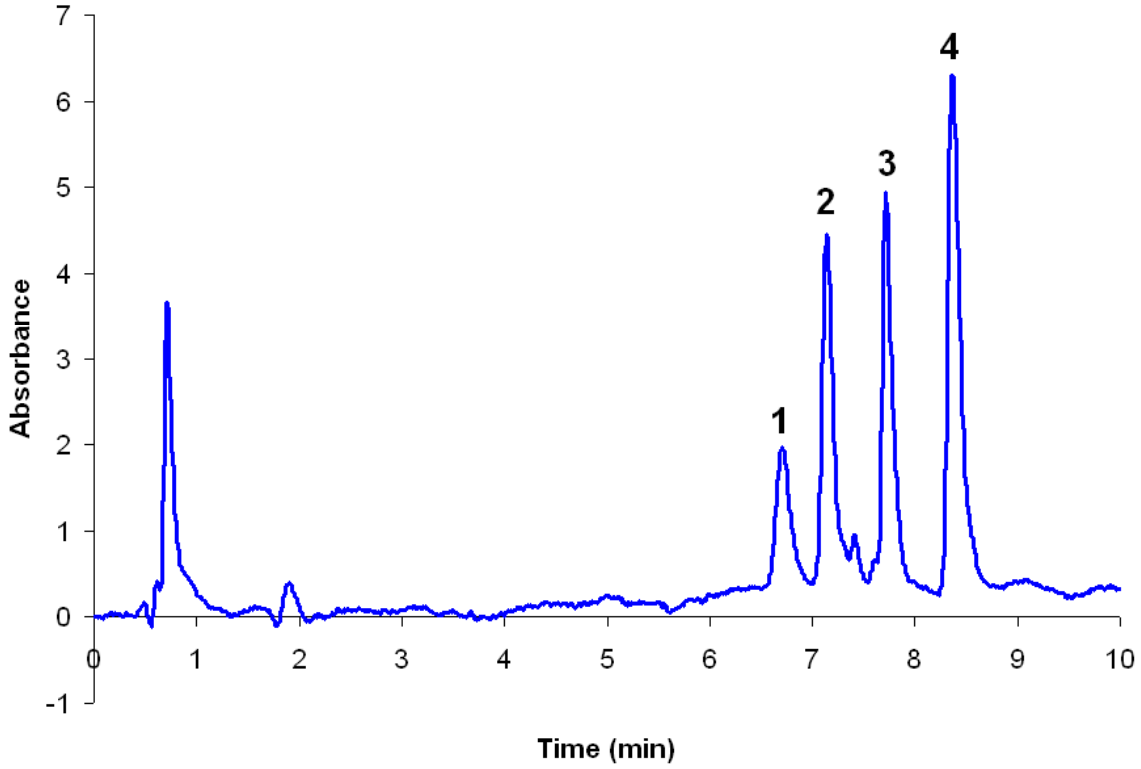
Porous morphology



Sharp edges



Separation of Proteins

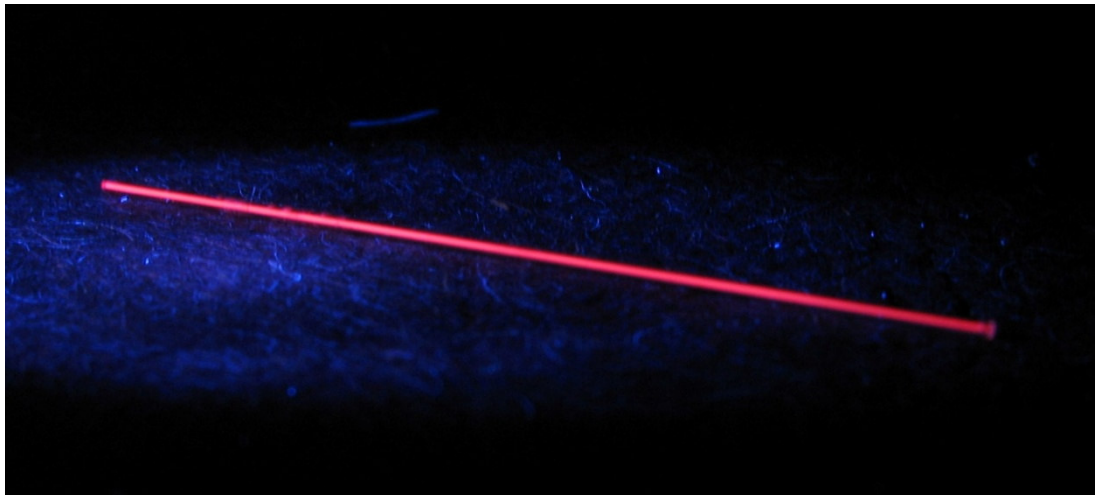


- Poly (BuMA-EDMA) monolith
- Flow rate = 1µl/min
- Detection = 210 nm
- Gradient = 0-60% ACN in 5 min

(1) Ribonuclease A (2) Cytochrome C (3) Myoglobin, (4) Ovalbumin

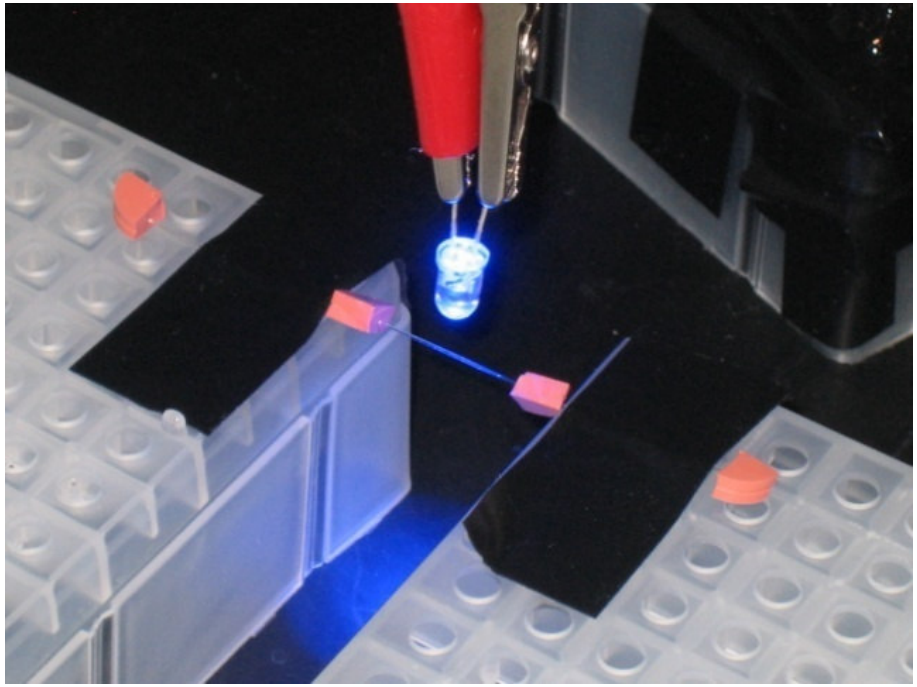
Other applications of the initiator

- Red light initiation system has also been used to graft chromophoric monomers onto monolithic scaffolds



Poly **(butyl methacrylate-*co*-ethylene dimethacrylate) with a spiropyran monomer grafted into the pores. The monolith is illuminated with a 375 nm LED to show the fluorescence of the spiropyran in the pores.**

Part II: Initiation at 470 nm



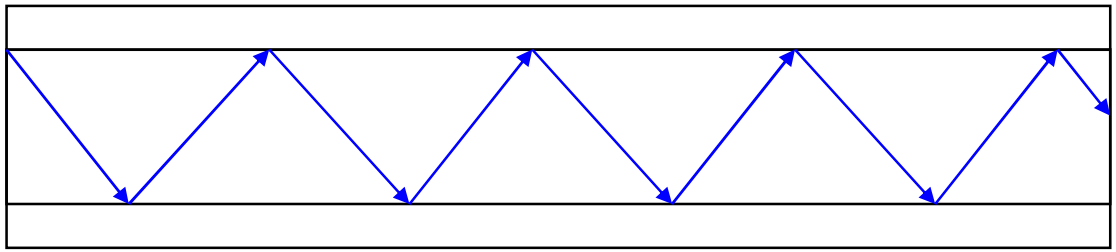
- Polymerisation of styrene-based monoliths within polytetrafluoroethylene coated capillaries with 470 nm LEDs and a camphorquinone/ethyl-4-dimethylamino benzoate initiator complex

If red works, why use blue?

- Red light can be used to initiate the more reactive methacrylate monomers
- Styrenes, however, are more stable and need more energy to start to polymerise
- Styrenes also absorb in the UV region so UV is not an option
- Blue is the highest energy light in the visible region so we use 470 nm LEDs to polymerise styrene and divinylbenzene

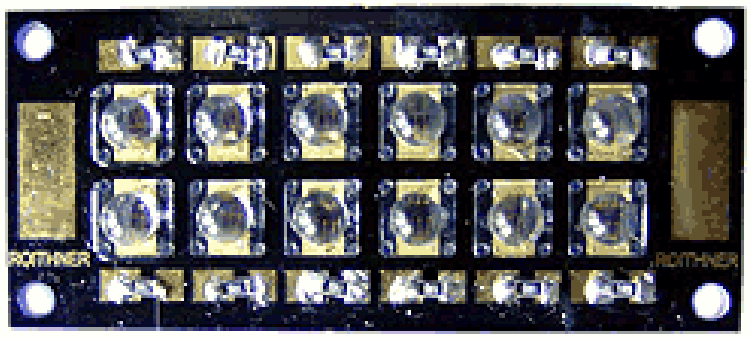
Position of the LED

- As PTFE coated capillary is a good waveguide the angle at which the LED is positioned is not important

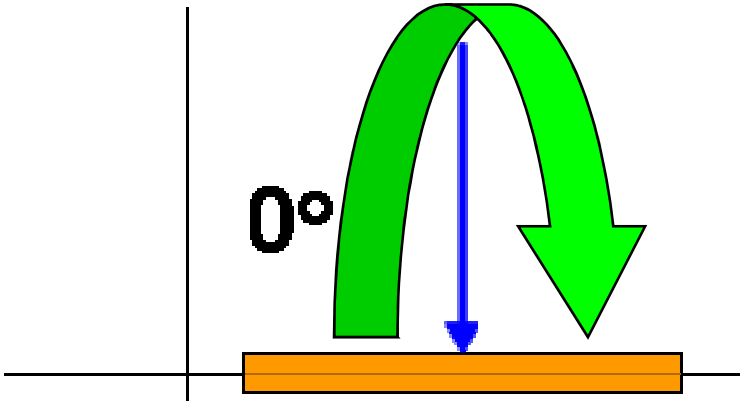


- Effective photo-masking can be a problem as light can travel under the mask
- Rubber septa were used as photo-masks for all the blue light experiments

LED arrays for longer columns

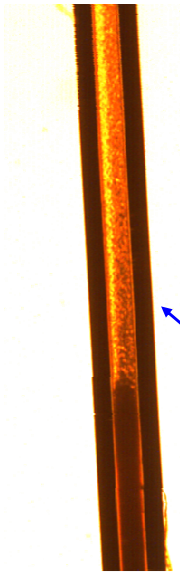


http://www.roithner-laser.com/LED_HP_multi_chip.html

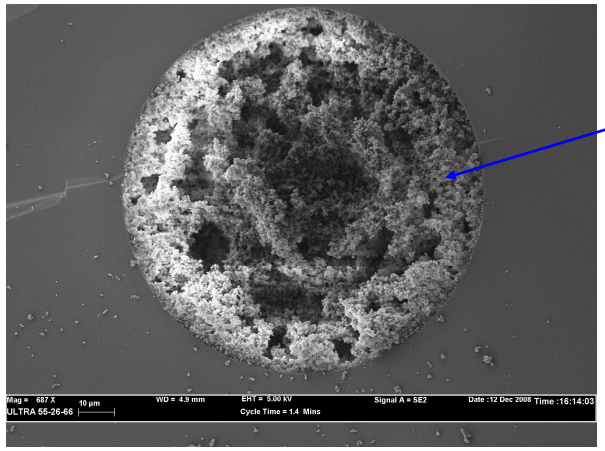


- When using the LED array, rotation is important as differences between light outputs from each LED produce column inhomogeneities
- Due to waveguiding when using single LEDs rotation is unnecessary

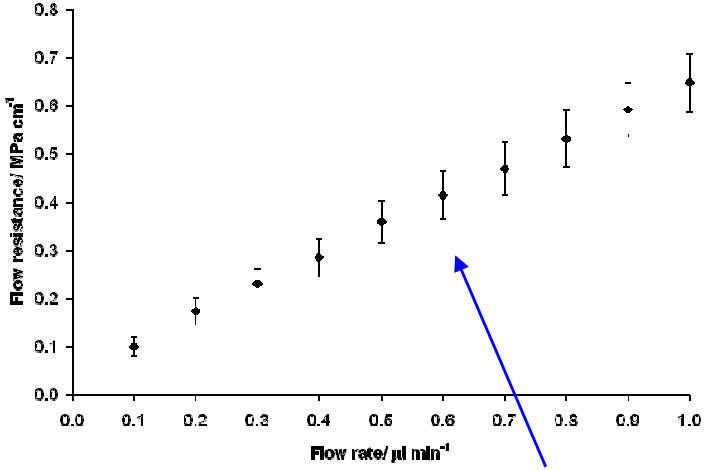
Characterisation of monoliths



Sharp edged monolith can be obtained with LED array using photo-masks

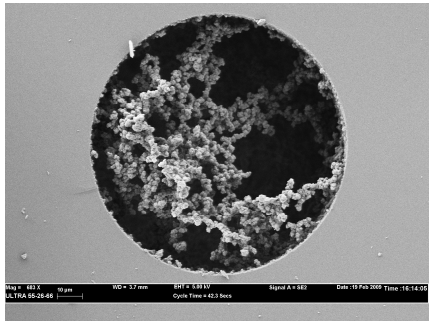


Polymerisation obtained with high-power LED array

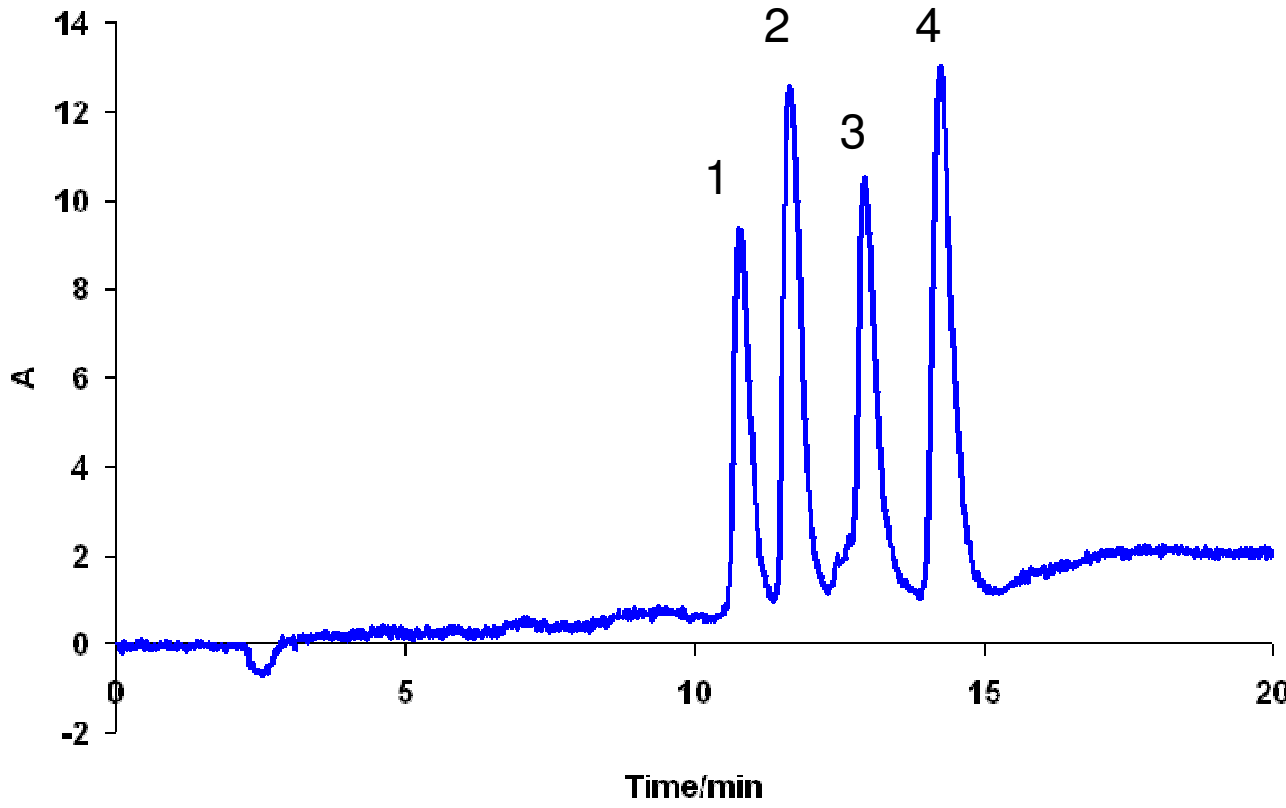


Low backpressure suggests good permeability

Polymerisation obtained with single low power LED



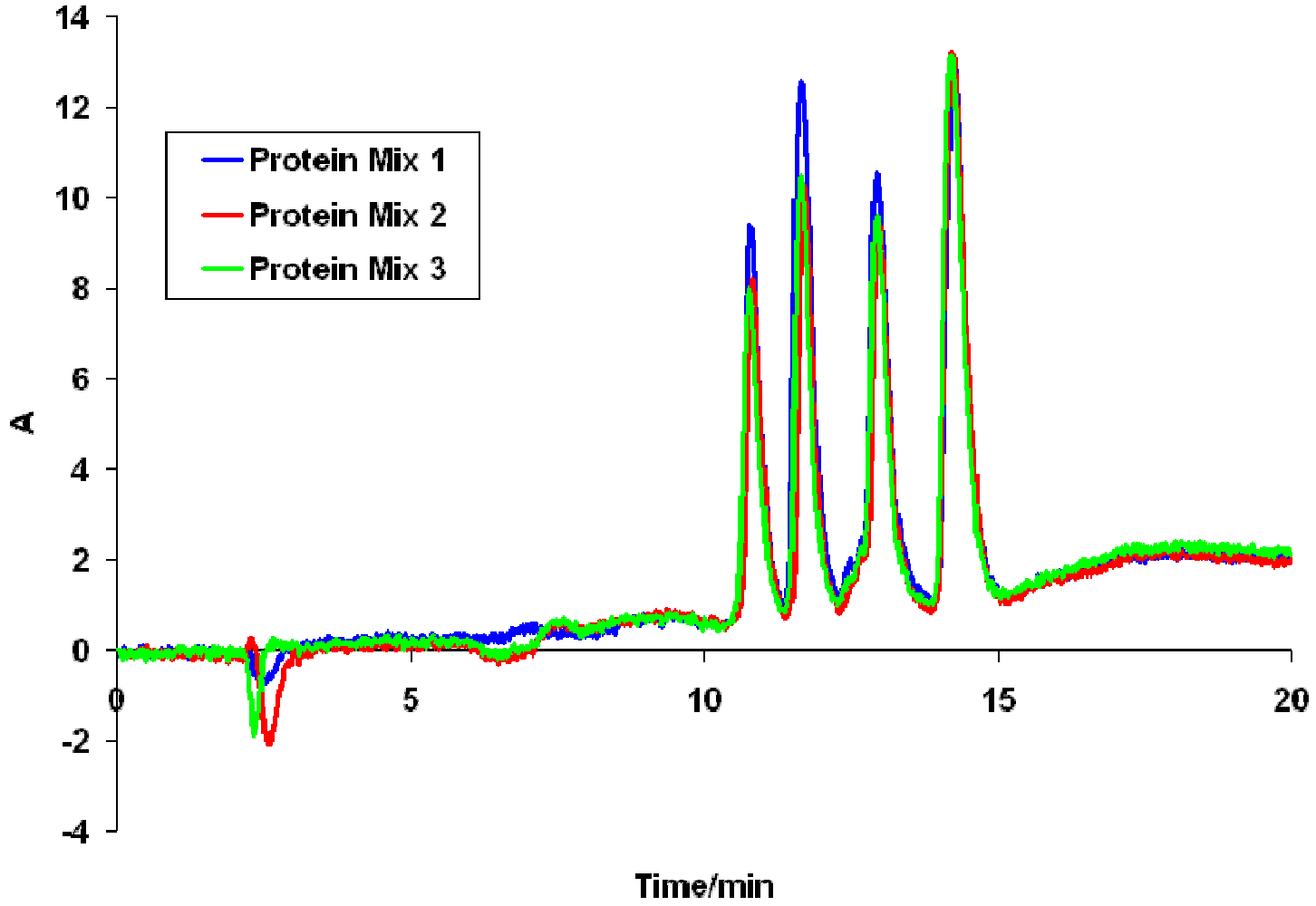
Separations



- Poly (S-DVB) monolith
- Flow rate = 1µl/min
- Detection = 210 nm
- Gradient = 0-60% ACN in 10 min

(1) Ribonuclease A (2) Cytochrome C (3) Myoglobin, (4) Ovalbumin

Reproducibility



Conclusions

- Successful synthesis of a range of methacrylate monoliths within polyimide coated fused silica capillary
- Grafting of a chromophoric spiropyran monomer onto the surface of a *poly* (BuMA-EDMA) monolith using red light
- Successful polymerisation of PS-DVB monoliths in PTFE coated capillary in the visible region using blue light

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- Dr. Marian Snauko
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- Materials Science Division at the Molecular Foundry
- All Separation Science Cluster at DCU
- CASSS organising committee for travel grant

Thank You For Your Attention


Questions?